

The Vaporization of B₂O₃(l) to B₂O₃(g) and B₂O₂(g) (Poster)

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The vaporization of B₂O₃ in a reducing environment leads to formation of both B₂O₃(g) and B₂O₂(g). While formation of B₂O₃(g) is well understood, many questions about the formation of B₂O₂(g) remain. Previous studies using B(s) + B₂O₃(l) have led to inconsistent thermodynamic data. In this study, it was found that after heating, B(s) and B₂O₃(l) appear to separate and variations in contact area likely led to the inconsistent vapor pressures of B₂O₂(g). To circumvent this problem, an activity of boron is fixed with a two-phase mixture of FeB and Fe₂B. Both second and third law enthalpies of formation were measured for B₂O₂(g) and B₂O₃(g). From these the enthalpies of formation at 298.15 K are calculated to be -479.9 ± 41.5 kJ/mol for B₂O₂(g) and -833.4 ± 13.1 kJ/mol for B₂O₃(g). Ab initio calculations to determine the enthalpies of formation of B₂O₂(g) and B₂O₃(g) were conducted using the W1BD composite method and show good agreement with the experimental values.

The Vaporization of $B_2O_3(l)$ to $B_2O_3(g)$ and $B_2O_2(g)$

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Vaporize $B_2O_3(l)$ in Reducing Environments

- Applications and need for thermodynamic data
 - Ceramic processing
 - Corrosion of high-temperature ceramics
- Two vaporization routes
 - $B_2O_3(l) = B_2O_3(g)$
 - $2/3 B$ (or other reductant) + $2/3 B_2O_3(l) = B_2O_2(g)$
- Approach [1]
 - Ab initio study using quantum chemical composite methods
 - Knudsen effusion mass spectrometry (KEMS) [2]

Previous Studies

- Thermodynamics of $B_2O_3(g)$ well understood, reliable data available
- Questions on $2B(s) + 1/2 O_2(g) = B_2O_2(g)$; issues with B and $B_2O_3(l)$ rxn

Investigator/method and reaction	$\Delta_f H_{298.15}^o$ kJ/mol—2 nd Law	$\Delta_f H_{298.15}^o$ kJ/mol—3 rd Law	$\Delta_f H_{298.15}^o$
Inghram (KEMS) [3]	-509.4	-444.1	
$2/3 B + 2/3 B_2O_3(l) = B_2O_2(g)$			
Inghram (KEMS) [3]	-455.2	-458.7	
$2/3 B + 2/3 B_2O_3(g) = B_2O_2(g)$			
Scheer (Torsion) [4]	-428.6	-462.9	
$2/3 B + 2/3 B_2O_3(l) = B_2O_2(g)$			
Rentzepis et al. (Collection) [5]	-466.2		
$C(s) + B_2O_3(l) = B_2O_2(g) + CO(g)$			
Searcy and Myers [6]	-458.9		
$2Mg(s) + 2B(s) = 2Mg(g) + B_2O_2(g)$			
Nguyen et al. (ab initio) [7]	-457.7		
$2B(g, doublet) + 2O(g, triplet) = B_2O_2(g)$			

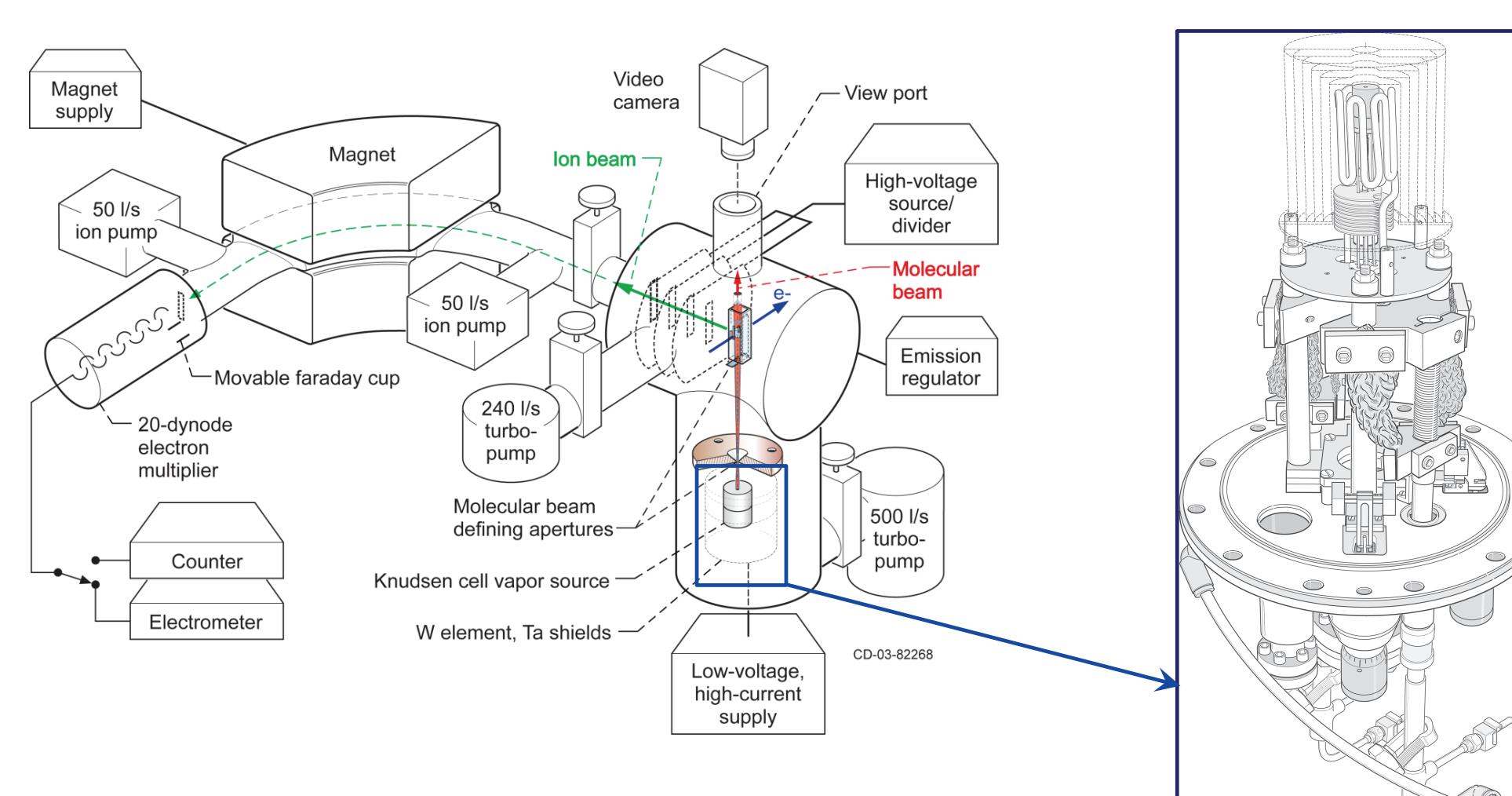
Theoretical Heats of Formation: Quantum Chemistry Composite Methods [8–12]

- Equilibrium geometry and frequencies computed at B3LYP/VTZ+1 level
 - Linear O-B-O shape for the $B_2O_2(g)$ and V shape for $B_2O_3(g)$
- W1BD Method, Gaussian Software [9,10]
 - Basis set: aug-cc-VnZ n = D,T, or Q
- Relativistic corrections/spin-orbit coupling effects included
- In the W1BD Modification of the W1 method, Brueckner Doubles used to simplify calculations
- Enthalpies of reaction determined from where all other reactants and products have known enthalpies of formation

Species/Reaction	W1BD Enthalpy/kJ mol ⁻¹	Nguyen et al. (7) Enthalpy/kJ mol ⁻¹
$B_2O_2(g)$		
$B_2O_2(g) = 2B(g, doublet) + 2O(g, triplet)$	-479.9 ± 17.2	-457.7
$B_2O_2(g) + 6HF(g) = 2BF(g) + 2H_2O(g) + H_2(g)$	-456.7 ± 5.3	
$B_2O_2(g) + 6H(g) = 2BH(g) + 2H_2O(g) + H(g)$	-441.1 ± 14.7	
$B_2O_3(g)$		
$B_2O_3(g) = 2B(g, doublet) + 3O(g, triplet)$	-857.4 ± 17.2	-830.1
$B_2O_3(g) + 6HF(g) = 2BF(g) + 3H_2O(g)$	-831.8 ± 5.3	
$B_2O_3(g) + 6H(g) = 2BH(g) + 3H_2O(g)$	-816.2 ± 14.8	

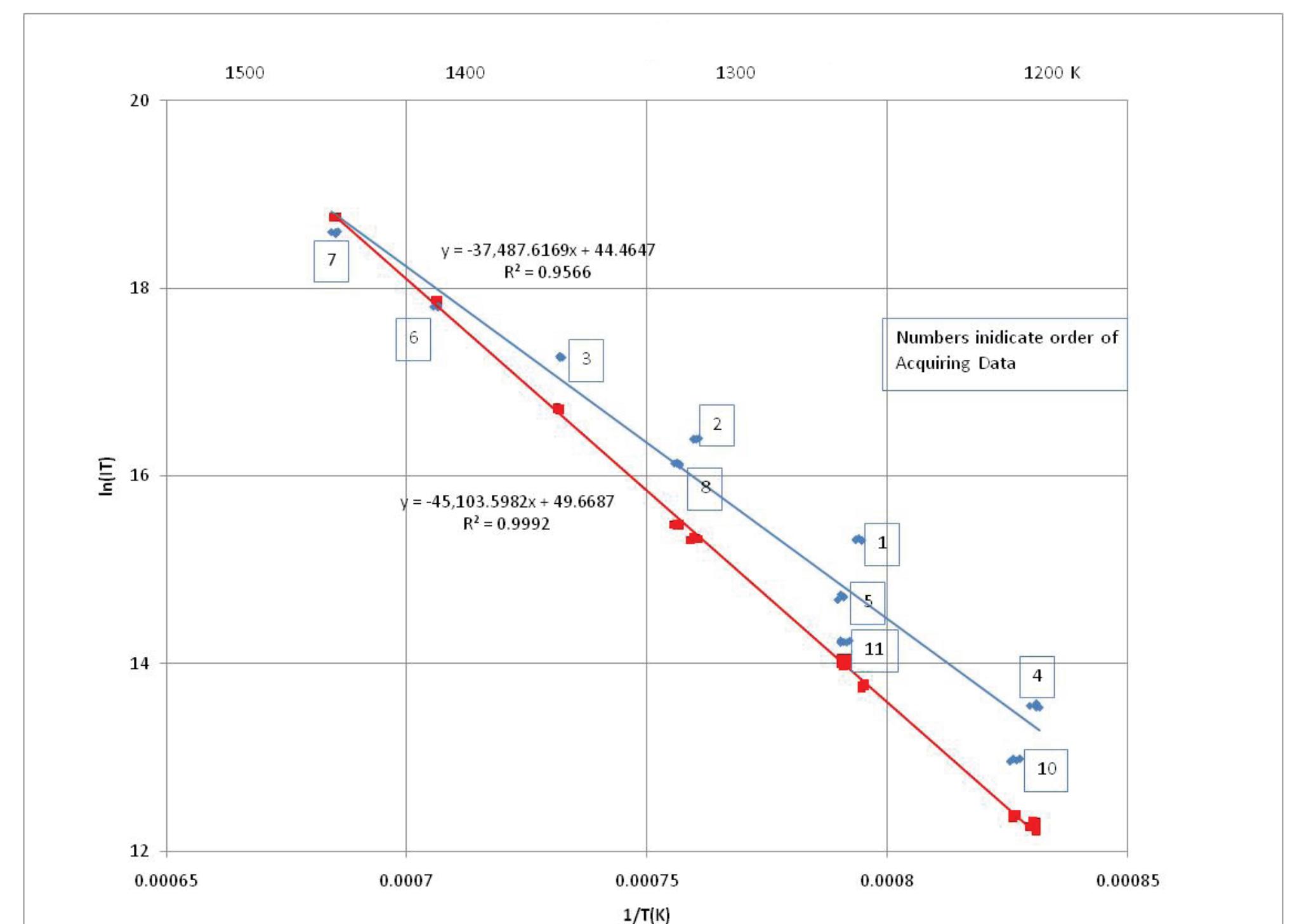
- Spin state is singlet, unless specified. Isogeric reactions (constant spin) preferred.

Glenn Research Center Knudsen Effusion Mass Spectrometer [2]



- Resistance heated cell
- Cross axis electron impact ionizer; 90° magnetic sector; and ion counting detector

B + B_2O_3 in BN Single Cell 11-1, 2, 3-10



Analysis of Data: Determine $\Delta_f H_{298.15}^o$

- Use heats of formation of other compounds:
 - $4/3 FeB(s) + 2/3 B_2O_3(l) = B_2O_2(g) + 2/3 Fe2B(s)$
 - $4/3 B(s) + O_2(g) = 2/3 B_2O_3(l)$ [16]
 - $4/3 Fe(s) + 4/3 B(s) = 4/3 FeB(s)$ [17]
 - $2/3 Fe_2B(s) = 4/3 Fe(s) + 2/3 B(s)$ [17]
- $2 B(s) + O_2(g) = B_2O_2(g)$
- Total error must include error in each of these heats

Summary of Data for $\Delta_f H_{298.15}^o B_2O_2(g)$

Investigator/Technique	Data Points	Average Temperature K	Enthalpy of Reaction	2B(s) + O ₂ (g) = B ₂ O ₂ (g)
Inghram et al. KEMS [3]	6	1400	302.5 ± 4.2	407.0 ± 7.2
$2/3 B + 2/3 B_2O_3(l) = B_2O_2(g)$			391.5 ± 0.7*	-509.4
Inghram et al. KEMS [3]	3	1410	103.1 ± 1.0	104.9 ± 1.1
$2/3 B + 2/3 B_2O_3(g) = B_2O_2(g)$			101.4 ± 0.3	-455.2
Scheer-Torsion [4]	14	1390	382.5 ± 2.2	326.2 ± 4.4
$2/3 B + 2/3 B_2O_3(l) = B_2O_2(g)$			372.7 ± 2.0	-428.6
Inghram et al. KEMS [3]	5	1390	232.0 ± 2.8	232.0 ± 2.8
$B_2O_3(l) + 3C + 2O_2(g) = 2B_2O_2(g)$			-466.2 ± 6.5	
Inghram et al. KEMS [3]	1	1375		-458.9 ± 16.7
$2Mg(s) + 2B(s) = 2Mg(g) + B_2O_2(g)$				-456.1 ± 8.4
JANAF [16]				-457.738*
IVTAN [18]				
This Study Run 1	8	1284	363.8 ± 2.8	384.9 ± 2.9
$2/3 B + 2/3 B_2O_3(l) = B_2O_2(g)$			411.6 ± 1.6	-488.0
This Study Run 1	8	1284	113.0 ± 2.1	115.6 ± 2.1
$4/3 FeB(s) + 2/3 B_2O_3(l) = B_2O_2(g)$			125.1 ± 0.8	-489.2
This Study Run 2	9	1280	376.7 ± 1.4	399.0 ± 1.5
$2/3 B + 2/3 B_2O_3(g) = B_2O_2(g)$			413.0 ± 0.9	-484.0
This Study Run 2	6	1280	122.5 ± 1.8	125.6 ± 1.8
$4/3 FeB(s) + 2/3 B_2O_3(l) = B_2O_2(g)$			125.8 ± 0.5	-479.0
This Study Run 3	9	1290	384.0 ± 1.5	405.5 ± 1.5
$4/3 FeB(s) + 2/3 B_2O_3(l) = B_2O_2(g)$			414.0 ± 0.7	-477.5
This Study Run 3	9	1290	123.6 ± 1.7	123.7 ± 1.7
$4/3 FeB(s) + 2/3 B_2O_3(g) = B_2O_2(g)$			126.0 ± 0.6	-481.1
				-478.6

*Inghram et al. only converted three points to pressure and hence only three points were used for the 3rd Law enthalpy.

*Given class of accuracy is 6-F, which means an uncertainty is ±40 kJ/mol

Summary of Data for $\Delta_f H_{298.15}^o B_2O_3(g)$

Investigator	Number of Data Points	Average Temperature T	B ₂ O _{3(l)} + B ₂ O _{3(g)}		2B(s) + 3/2 O ₂ (g) = B ₂ O _{3(g)}			
			2 nd Law	2 nd Law	3 rd Law	From 2 nd Law	From 2 nd Law	Tables
Hildenbrand-Torsion [19]			302.5 ± 4.2	427.5	417.3	+82.9	-93.0	
Scheer-Torsion [20]	14	1500	364.9 ± 3.8	405.2 ± 3.9	424.2 ± 0.9	-848.2	-829.2	
Shultz et al.—mass spectrometry and weight loss [21]	14			412.1 ± 8.4	415.5 ± 0.1			-836.0 ± 4.2
JANAF [16]								-836.383*
IVTAN [18]								
This Study—B ₂ O ₃ only	11	1320	380.8 ± 1.2	410.7 ± 1.3	425.5 ± 1.2	-842.6	-823.9	
This Study—FeB, B ₂ O ₃	8	1270	373.2 ± 1.7	401.7 ± 1.8	426.7 ± 1.7	-851.7	-824.7	
This Study—Run 2	6	1225	380.8 ± 1.7	409.9 ± 1.7	430.3 ± 1.3	-843.5	-823.1	
This Study—Run 3	9	1290	389.0 ± 1.3	417.9 ± 1.3	430.9 ± 0.8	-855.5	-822.5	

Conclusions

- Theoretical and experimental determination of heat of formation of $B_2O_2(g)$ and $B_2O_3(g)$
- Theoretical: Quantum chemistry composite method
- Experimental: Use Fe_2B/FeB mixture to set B activity, gave more reliable results than B alone
 - For $B_2O_2(g)$ $\Delta_f H_{298.15}^o = -479.9 \pm 25.7$ kJ/mol
 - For $B_2O_3(g)$ $\Delta_f H_{298.15}^o = -833.4 \pm 13.1$ kJ/mol

References

- Jacobson, N. S.; Myers, D. L. <i